Quarterly Progress Report

For Period

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FUNDAMENTAL STUDIES OF THE METALLURGICAL,
ELECTRICAL, AND OPTICAL PROPERTIES OF
GALLIUM PHOSPHIDE

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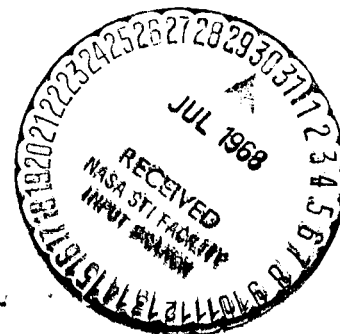
PROJECT 5112: THE PROPERTIES OF RECTIFYING JUNCTIONS IN GaAs$_x$P$_{1-x}$

The purpose of this project is to study the preparation and characterization of rectifying junctions in GaP and GaAs$_x$P$_{1-x}$. In particular, we wish to relate the structure of the crystals to the electrical properties of the junctions. During this quarter we have extended our study of the variation of p-n junction depth with diffusion time for zinc diffusion into gallium phosphide. We have also constructed a vertical liquid epitaxial system.

A. Diffusion of Zinc into Gallium Phosphide

Last quarter[1] we noted that when Zn is diffused into n-type GaP from a system containing liquid "a" and low phosphorus overpressure, the resulting p-n junction depth, x_j , is proportional to the square root of diffusion time only for shallow junctions. After the junction passes a critical depth, the zinc diffusion speeds up; and the resulting junction depths are deeper than would be predicted by $x_j \propto \sqrt{t}$.

We have now found that the same effect occurs when the diffusion system contains liquid "b" and high phosphorus overpressures. This is shown in Fig. 1. The p-n junction depth, x_j, and the depth of the shallower junction that is always revealed by the etchant, x_j' , are plotted against the square root of time. The results from diffusions done with liquid "a" are included for comparison. All diffusions were performed at 900°C.

There are several noticeable similarities between diffusions with liquid "a"and diffusions with liquid "b". For diffusions below the knee in the x_j versus $\sqrt{t}$ curve, the diffused crystals remain transparent and no induced defects are seen. Also, in analogy with Ting's work in GaAs,[2] the zinc concentration probably decreases smoothly with distance into the crystal . Above the knee the crystals are

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opaque (indicating heavy zinc precipitation), and induced dislocations are seen throughout the diffused layer. In analogy with GaAs, the zinc concentration probably stays relatively constant throughout much of the diffused layer and then decreases sharply.

The correlation between diffusion induced dislocations and enhanced diffusion is apparent. The dislocations do not form as soon as diffusion begins; they form only after the combination of zinc concentration and concentration gradient place a sufficient amount of strain on the GaP lattice. Once the dislocations have formed, the dislocation cores and the dilated regions near the dislocations can act as paths of easy diffusion for the interstitial species that dominates zinc diffusion. Provided the dislocations are in high enough concentration, the average diffusion in the entire layer is noticeably enhanced. Since the shape of the diffusion profile depends on phosphorus overpressure, it is not unexpected that the critical depth also depends on phosphorus overpressure.

B. Liquid Epitaxy

A vertical liquid epitaxial system has been constructed. The principles of operation for this system are the same as those for the horizontal system that was previously used. Only the geometry is different. In the vertical system, a solution of gallium saturated with phosphorus is held in a graphite crucible. To initiate crystal growth, a seed is lowered into the solution, and the solution is cooled. Growth is terminated when the seed is withdrawn.

This system will be used to study the distribution coefficient and electrical properties of Be in liquid epitaxial layers of GaP. For these purposes, the vertical system has two major advantages over the horizontal system. Because of the geometry, we are assured that the Be will be completely dissolved by the Ga solution. Also, because the seed may be withdrawn, the epitaxial layer may be grown over a narrow temperature range.

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2. C. H. Ting, Quarterly Status Report, Stanford Electronics
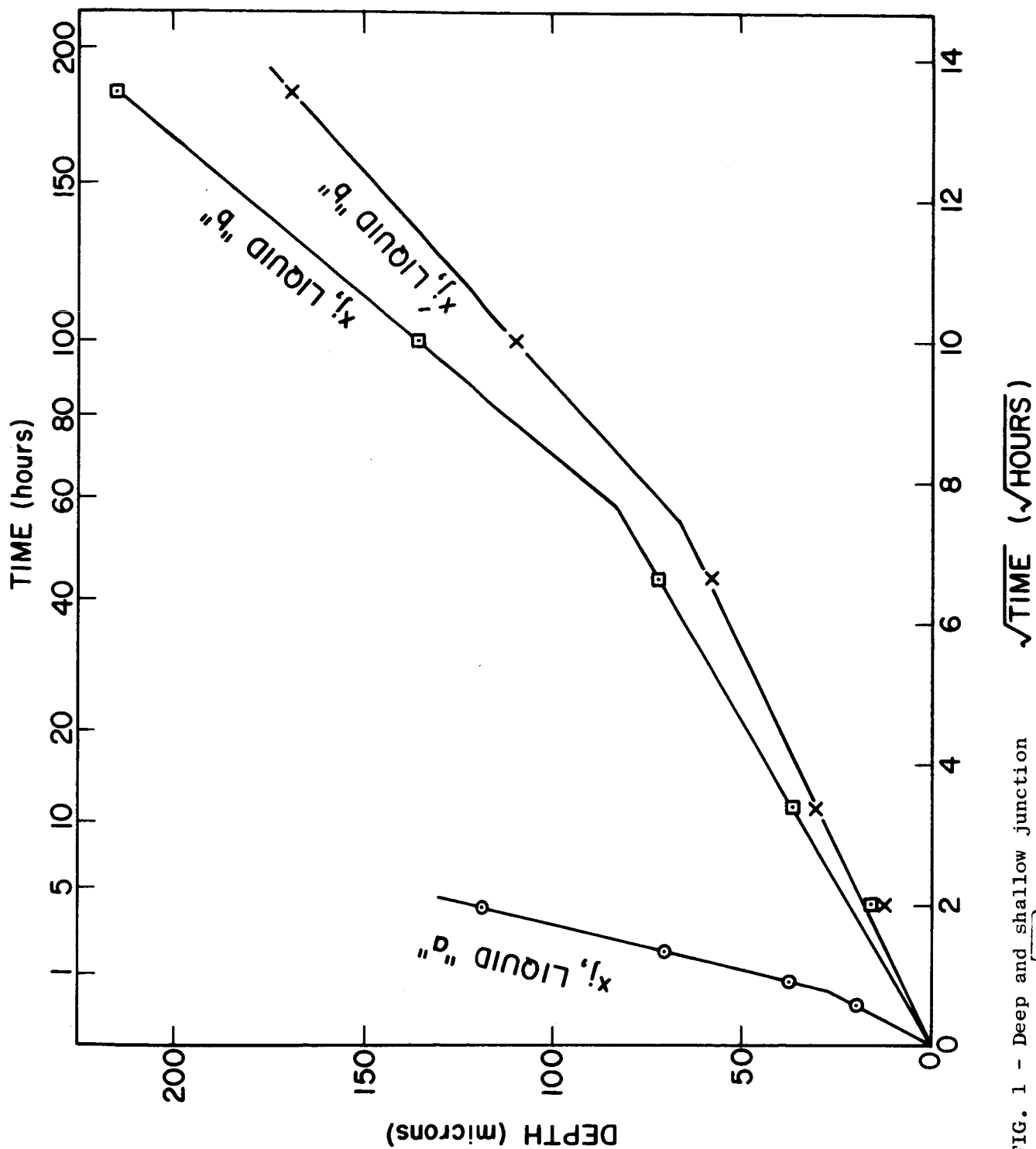   Laboratories, July 1 through September 30, 1967.

FIG. 1 - Deep and shallow junction
depths versus √time for liquids
"a" and "b", 900°C.

PROJECT 5115: SEMICONDUCTOR DEVICES FOR HIGH TEMPERATURE USE

National Aeronautics and Space Administration
Grant NsG-555
Project Leader: G. L. Pearson
Staff: Y. Nannichi

The purpose of this project is to prepare power rectifiers and solar batteries which will operate at temperatures up to $500^{\circ}C$. The current-voltage characteristics of metal:n-GaP Schottky barrier diodes have been studied. Some photoelectric responses were also measured. New processes are being adopted to improve the characteristics of these two types of devices.

A. Liquid-Epitaxial Crystals

Sn-doped crystals were grown on undoped GaP seeds to make ohmic contacts and to furnish mechanical support as indicated in our previous report.

Five crystals were successfully grown out of a 50 weight percent Sn-doped Ga solution after several unsuccessful attempts to grow out of a pure Sn melt. The electron concentrations are lower than we had expected from the data in the previous quarterly report. The cause of the failure to grow crystals out of a pure Sn melt was the formation of a crust on the surface of the melt arising from an impure He atmosphere in our present system. We plan to grow more heavily Sn doped crystals in order to reduce the series resistance.

B. V-I Characteristics

In the previous report we indicated that n, the slope of the ln I versus V curve, was 1.5. During this quarter we reduced the value of this slope to 1.05 which indicates less interface damage at the Schottky junction.

This improvement resulted from the following new surface treatment: the GaP crystal was lapped with #1200 grit, mechanically polished to a mirror-finish and etched for $1 \sim 2$ minutes just before placing in the evaporator. Before evaporating, the sample was heated at $400^{\circ}C$ for 30 minutes in a vacuum of less than 2×10^{-6} mm Hg. It was also

interesting to note that the derivation from a linear relation which
was observed below V = 0.5, supposedly due to surface leakage (see
Fig. 2 of the last quarterly report), was not observed with the sample
treated as above. Figure 1 compares the forward characteristics of our
improved diode with that of a previous leaky diode.

The surface was also treated by ion bombardment at 4 kV in an argon
atmosphere of 25 μ Hg. Due to structural limitations, we were forced to
break the vacuum between ion bombardment and evaporation in order to
insert a mask. The results were unsatisfactory and the experiment
will be repeated with improved techniques.

The differential forward resistance was as low as 25 ohms which
corresponds to a high resistive GaP layer about 15 μ in thickness.
This value is lower than that reported last quarter (200 ohms).

Figure 2 shows the reverse characteristic of this same diode. The
breakdown voltage was above 200 V, but appreciable surface leakage
current flowed at high voltages prior to breakdown. A mesa etching
technique to improve the characteristic was tried but this was
unsuccessful due to the lack of a suitable etching solution. Since
mesa etching should solve the edge breakdown problem, we will try to
find suitable etchants.

C. Photo-Response of the Schottky Diodes

The photo-response of a Schottky barrier diode was measured at
photon energies near the band gap. Either nickel or chromium was
chosen to form the semi-transparent film. Chromium, however, seemed
to be the preferable metal since it has a higher electrical conductivity
and reacted less with GaP and oxygen at high temperatures. Chromium
was electrochemically deposited on a tungsten filament and then
evaporated on to the surface of the prepared surface of the GaP single
crystal. The experiment was rather preliminary and no special care
was taken to increase the transparency of the metal film. The
transmittance of a film simultaneously deposited on glass was below
3 percent in the wavelength region where our study was made.

The photocurrent and photovoltage were measured at various temperatures in a vacuum of the order of one micron. The light source was an Xe lamp from which monochrometic light was obtained with a Bausch and Lomb grating monochrometer. Figure 3 shows the spectral photo-response at various temperatures between 20 and 400°C. The shift of the curve is mainly due to a change in the band gap with temperature which has been reported to be -5.5×10^{-4} eV/deg.

Figure 4 shows the photo-response at 2.85 eV (one of the strongest emission lines from the Xe lamp) versus temperature. Photocurrent has a maximum at about 200°C and the photovoltage decreases with increase in temperature at a rate of 1.2 mV/degree.

D. Non-ohmic Contacts

When one grows purer and purer materials, the problem of making ohmic contacts arises.[1] Though the GaP which we now use is not pure enough to cause this problem, the GaAs produced in our laboratory for another project (K702) has shown nonohmic contact behavior. We are carrying out experiments to find the cause of the nonohmic contacts on this GaAs.

We took the spectral photo-response of such a GaAs nonohmic contact at 77 and 300°K and found a peak about 30 meV below the band gap energy. It is too early to be certain but it seems that Si acceptor levels are responsible for the non-ohmicity.

The measured acceptor level of Si is 30 meV above the valence band.[2] Transition of donor Si atoms to acceptor sites would take place if the number of As vacancies should increase during the process of making ohmic contacts. A rather wide high resistance region just below the contacts can also be postulated in terms of a rapid diffusion of As vacancies. Further experiments are planned to clarify this problem.

E. Plans for the Next Quarter

More heavily doped n-type crystals will be grown to reduce the forward resistance. Mesa etching techniques will be more intensively studied. Diodes will be maintained at high temperature for long

periods of time to check for deterioration in their electrical and optical properties.

TABLE 1

Properties of Sn Doped GaP Layers Grown by Liquid Epitaxy

	Seed	Growth Temp($^{\circ}$C)	Thickness (μ)	Electron Conc. (cm^{-3})
LG12	CT1	845	30	1×10^{18}
LG13	VG4	900	30	0.8×10^{18}
LG14	#24	950	55	1×10^{18}
LG15	CT4	950	45	1×10^{18}
LG16	CT7	950	45	1×10^{18}

REFERENCES

1. Y. Nannichi, et al, Solid State Electronics, 10, 223 (1967).

2. O. Lorimor and W. Spitzer, J. Appl. Phys. 37, 3687 (1966).

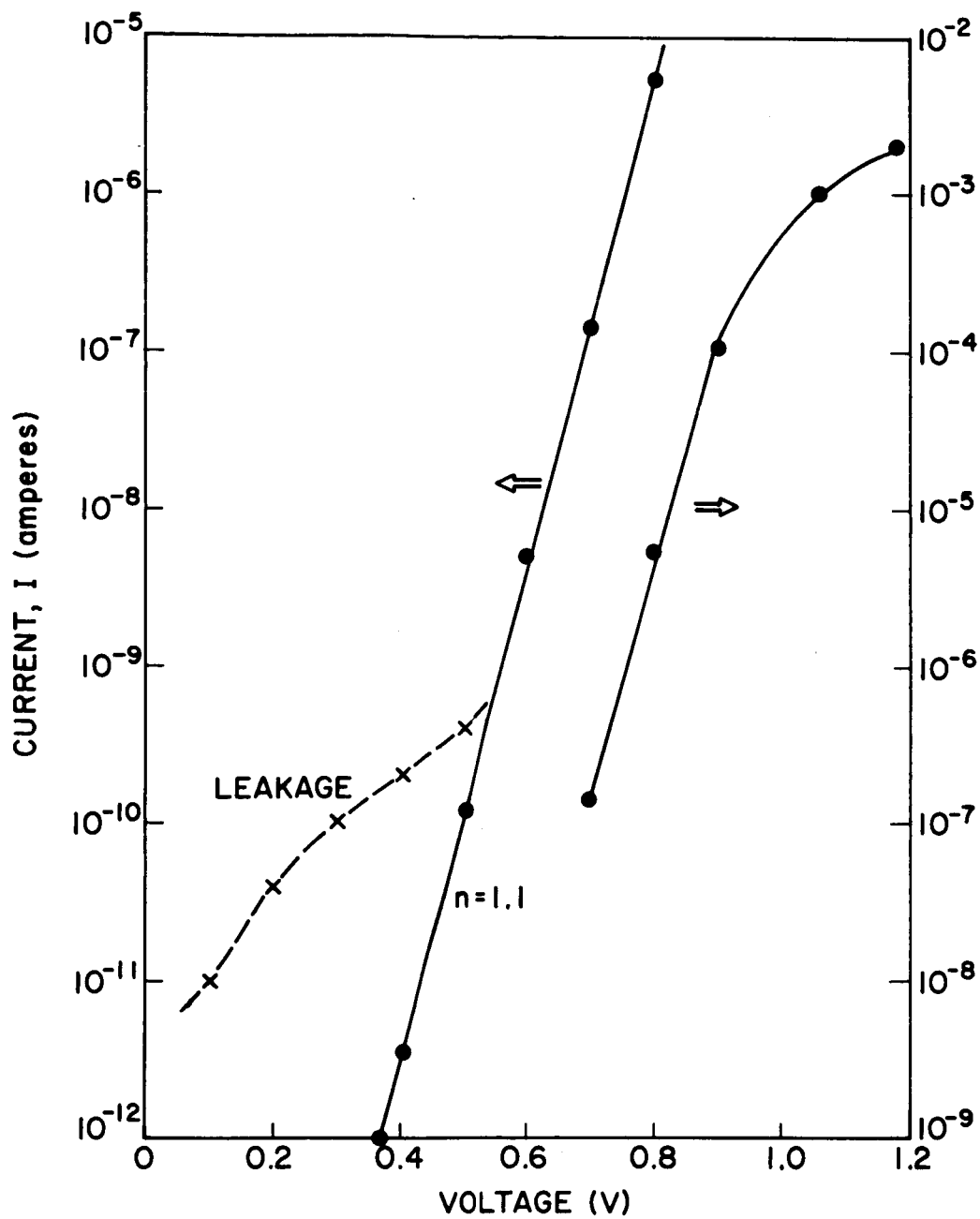FIG. 1 - Improved Forward Characteristics
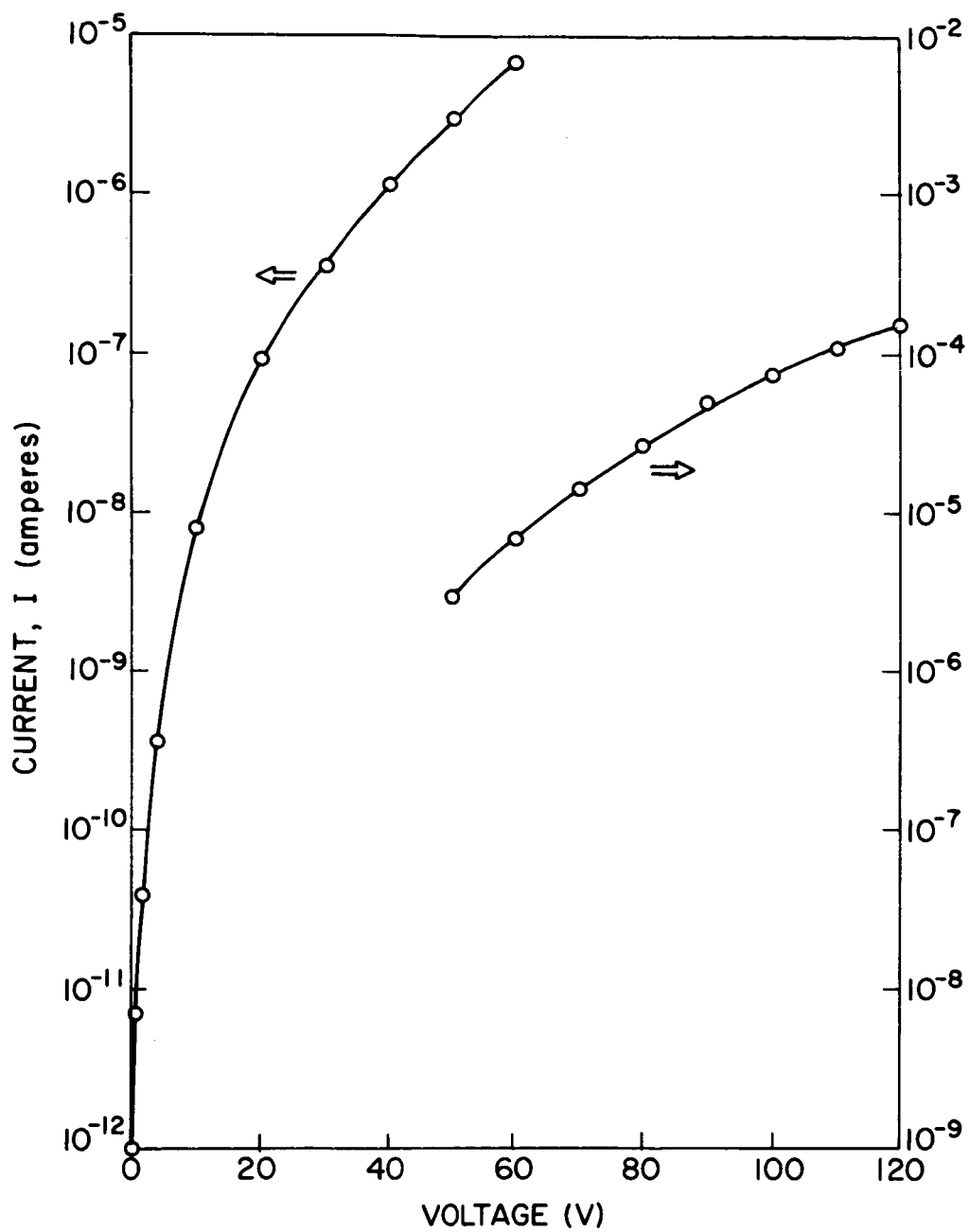of a GaP Schottky Diode.

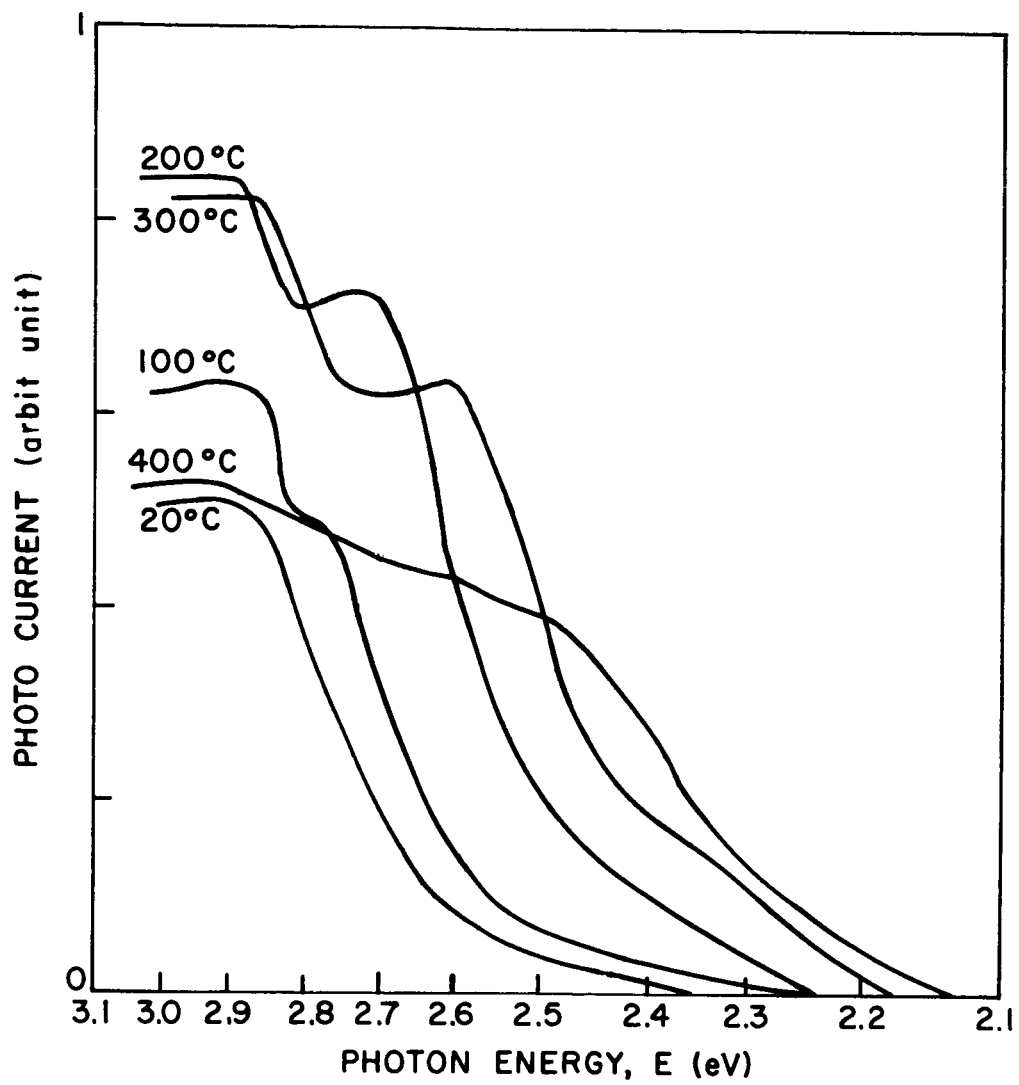FIG. 2 – Reverse Characteristics of a
GaP Schottky Diode.

FIG. 3 - Spectra Response of Photocurrent
of a Cr:n-GaP Schottky Diode.

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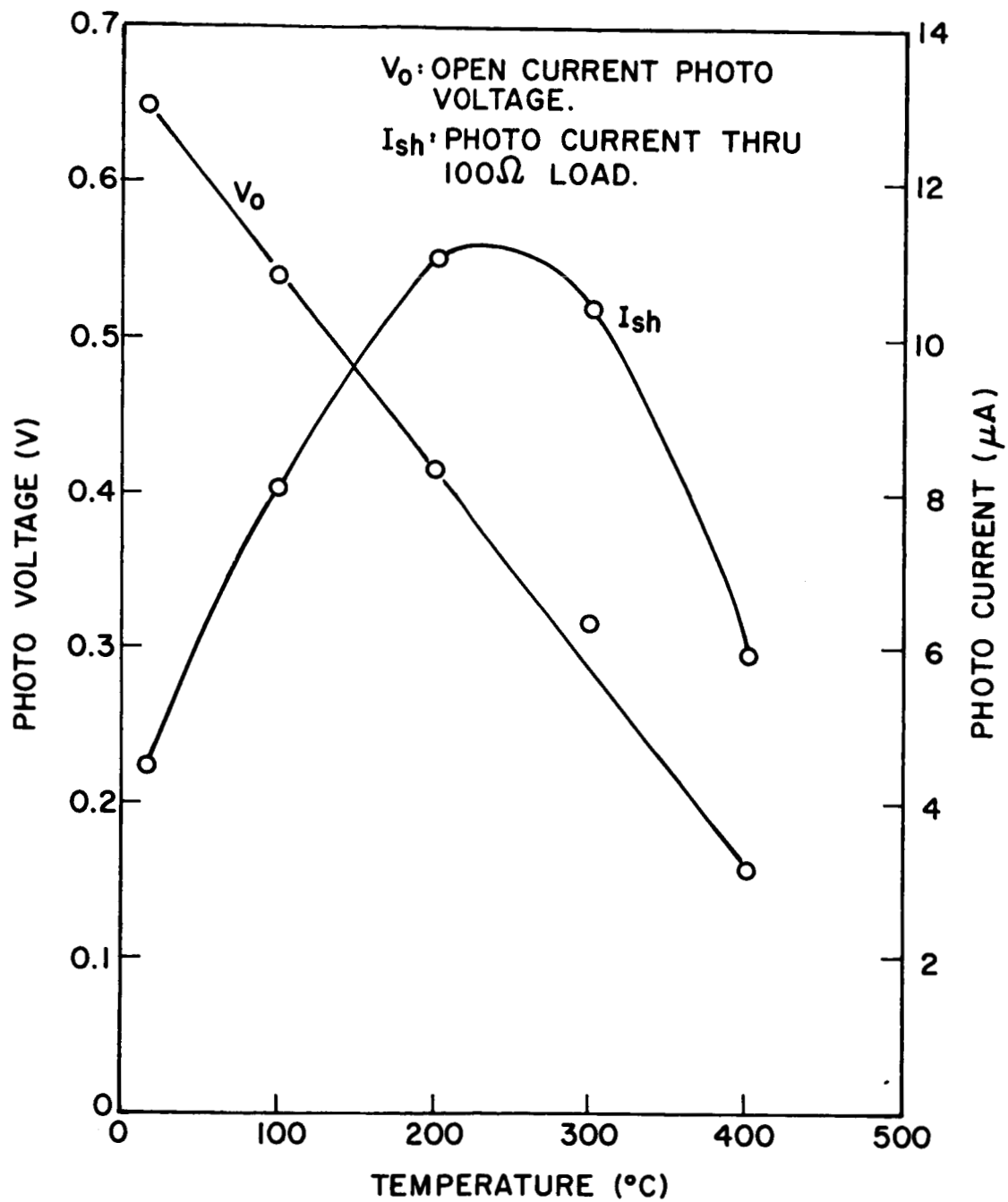FIG. 4 - Photo-response verus
Temperature.

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PROJECT 5116: DONOR IMPURITIES IN GaP

National Aeronautics and Space Administration
Grant NsG-555
Principal Investigator: G. L. Pearson
Staff: A. Young*

The purpose of this project is to study the behavior of shallow
donors in gallium phosphide. In particular S, Se, and Te will be
diffused into GaP to determine solubility and diffusion parameters.
This information will be useful in delineating the properties of GaP
doped with these shallow donor impurities.

Diffusion of Sulfur in GaAs

During the last quarter we have studied the diffusion of sulfur
in GaAs as a function of temperature, sulfur pressure, and arsenic
pressure. The purpose of this work was to compare previous results
obtained from our work of sulfur in GaP with the results for GaAs.
Of particular interest were the dependence of sulfur surface concentra-
tion on sulfur pressure and the dependence of diffusion coefficient
on the arsenic or phosphorus pressure. For comparison, previous
results for sulfur in GaP are listed below

$$\text{surface concentration (solubility)} \qquad C_s \sim P_{s_2}$$

$$\text{diffusion coefficient} \qquad D \sim (P_{p_2})^0 = \text{independent of pressure}$$

Variation of Diffusion Coefficient with Arsenic Pressure

The diffusion coefficient of sulfur in GaAs was studied as a
function of arsenic pressure with a fixed sulfur vapor density of
0.2 μg/ml at 1003°C and 1130°C. The diffusion profiles obtained from
radiotracer measurements were fitted with complementary error functions.
The values of D are plotted in Fig. 1 as a function of arsenic
pressure. The diffusion coefficient appears to be independent at
pressure in the high pressure region above 0.5 ATM. Below the

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knee, the diffusion coefficient varies as

$$D \sim (P_{As_4})^{1/2} \quad .$$

Qualitatively similar results were obtained for silicon[1] and sulfur[2] in GaAs using p-n junction techniques. In the case of sulfur, however, the drop-off below the knee was much sharper than observed here.

The cause of the knee is not known. Vieland[2] has suggested the possibility of two diffusion mechanisms - one dominant at high arsenic pressures, the other at low pressures. This seems to be a reasonable suggestion but cannot account for the shape of the observed curve.

Kendall has suggested a model that can explain the shape of the D versus P_{As_4} curve.[3] This mechanism would be operative if $[V_{As}^{+}] = [V_{Ga}^{-4}]$ were the dominant charge neutrality condition, and if the diffusion defect involved V_{Ga}^{-}. However, the functional dependence on pressure below the knee is much smaller than our observed 1/2 power.

The observed saturation of D at high pressures could be caused by the appearance of a phase boundary - e.g., the solidus boundary and the presence of an arsenic-rich liquid. However, the pressures at the solidus boundary as determined by Thurmond[4] are an order of magnitude larger than the pressures at the knee.

Another possibility is a limitation of the rate of equilibrium of the crystal with the external environment. As suggested by Schottky[5] equilibration may be slow in low dislocation crystals. (Our crystals have etch pit densities of 1-2000/cm^2). It may also be a function of arsenic pressure. Kendall[6] indicated that the surface concentration of radioactive arsenic in GaAs (at P_{As_4} = 1 ATM) was very slow in building up to its equilibrium value at 1200°C, reaching a mole fraction of only 10^{-5} radioactive arsenic after 4 hours. This suggests the existence of a severe rate limiting process for arsenic from the gas phase into the crystal at this pressure. It is interesting

to note that the diffusion coefficient of zinc in GaAs also behaves anamalously at pressures above 2 ATM.[7]

The D versus P_{As_4} curve for 1003^OC was repeated. However, in this case, the samples were preannealed for 5 days at 1003^OC under the appropriate arsenic pressures. They were then diffused with sulfur-35 under arsenic pressure for 12 hours. The results in Fig. 1 show a slight decrease in junction depth (15%), but the shape of the curve remains the same. Thus it is unlikely that a rate limitation of equlibrium with the arsenic vapor is responsible for the knee.

It may seem strange that the diffusion of sulfur (believed to be substitutional on the sublattice) is enhanced by higher arsenic pressures. A possible explanation is that of Woodbury's "covacancy" mechanism[8] - essentially an interchange mechanism between arsenic sites which is enhanced by the presence of a vacancy on the other sublattice.

Variation of Surface Concentration (Solubility) with Sulfur Pressure

Sulfur was diffused into GaAs at 1003^OC and 1130^OC at a fixed arsenic pressure above the knee of the D versus P_{As_4} curve. The diffusion profiles are shown in Figs. 2 and 3 for various sulfur pressures. The profiles at 1130^OC appear to be well-behaved except for a few points near the surface. If a smooth extrapolation is made from the rest of the profile to the surface, the surface concentration is found to be proportional to the sulfur pressure, in agreement with our results for GaP at 1215^OC.

At 1003^OC, the surface concentration at the lower sulfur pressure appears to be much less dependent on sulfur pressure than at 1130^OC. At the highest sulfur pressure used, the profile is not well-behaved, as with GaP.

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4. C. D. Thurmond, J. Phys. Chem. Solids, $\underline{26}$, 785, (1965).

5. G. Schottky, J. Phys. Chem. Solids, $\underline{27}$, 1721 (1966).

6. D. L. Kendall, Ph.D. Dissertation, Stanford University, Department of Materials Science, 1965, p.41.

7. K. K. Shih, et al, J. Phys. Chem. Solids, $\underline{29}$, 379 (1968).

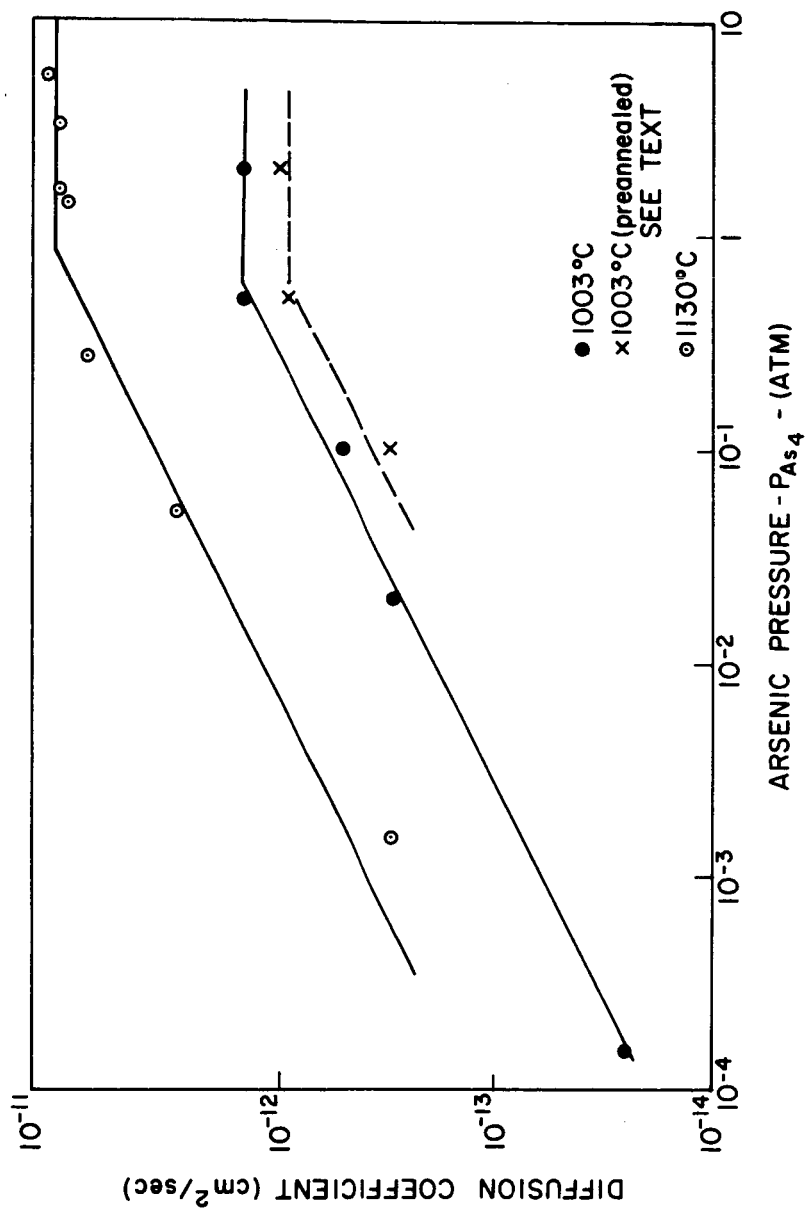8. H. H. Woodbury, Phys. Rev., $\underline{134}$, A492 (1964).

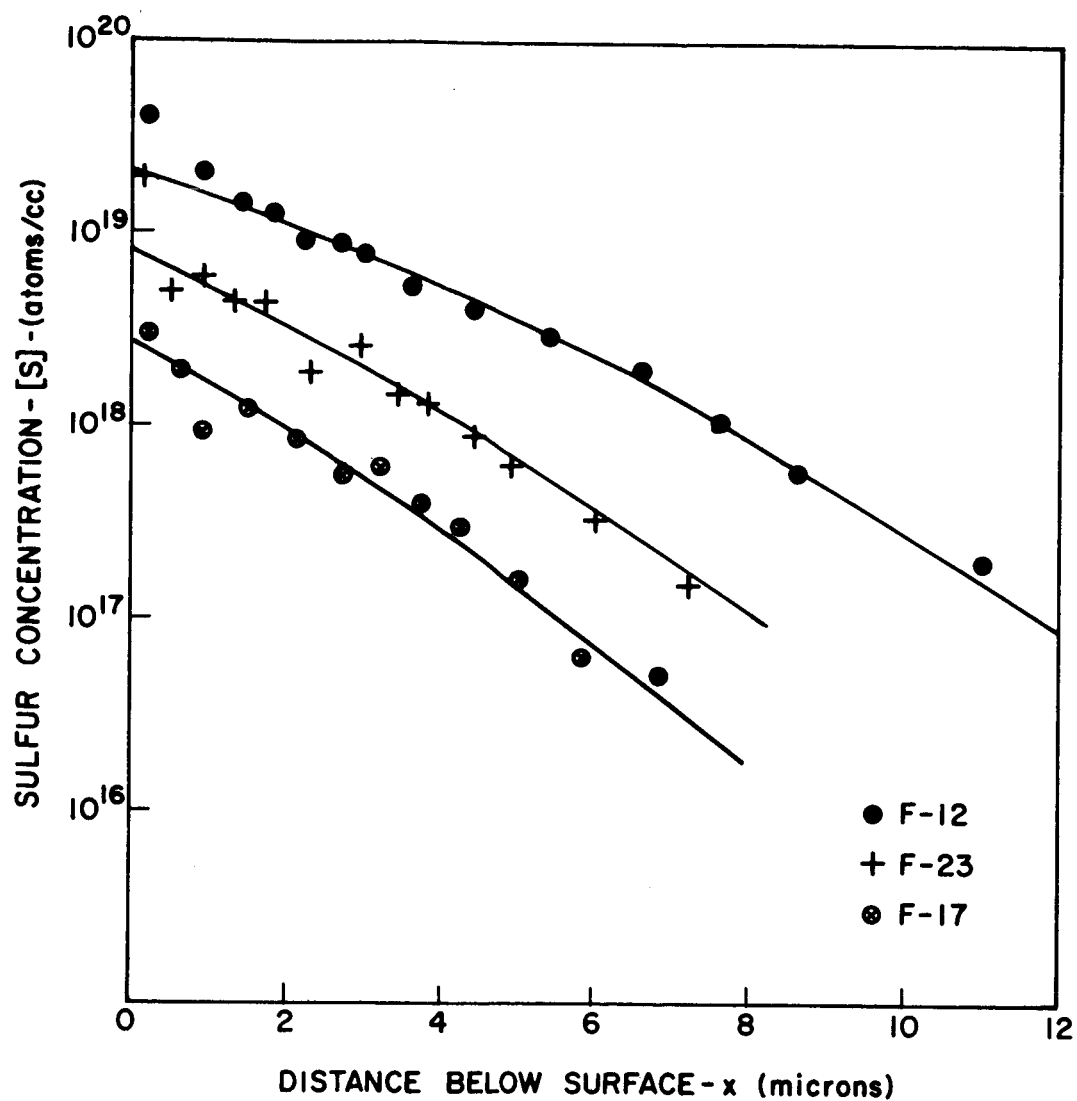FIG. 1 – Variation of Diffusion Coefficient with Arsenic Pressure (sulfur in GaAs).

FIG. 2 - Sulfur Profiles in GaAs at
1130°C for Varying Sulfur Pressures
t = 1 hour [As] = 4.5 mg/ml,
[S]: F-12, 2 µg/ml; F-23, 0.6 µg/ml;
F-17, 0.2 µg/ml.
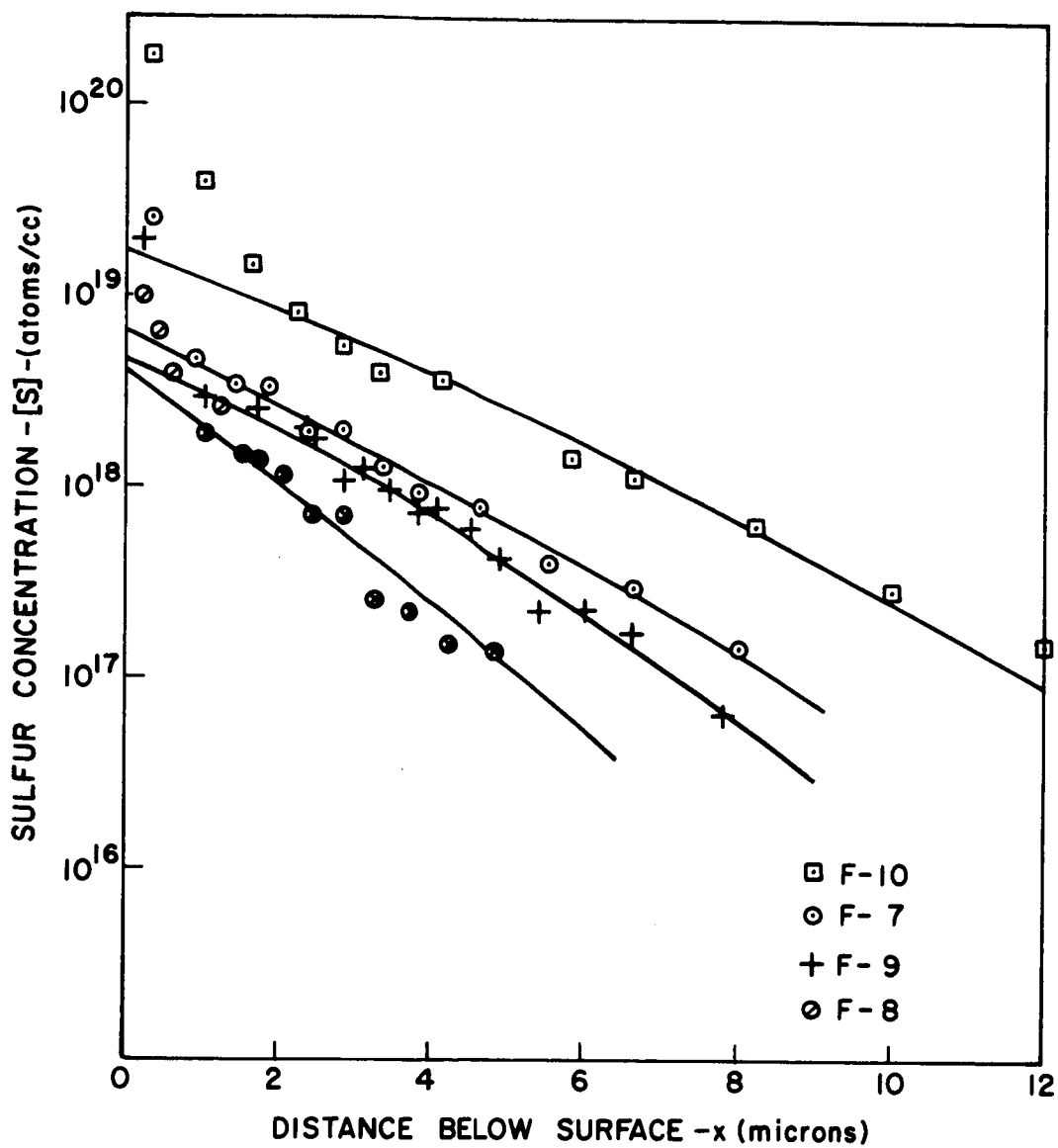
FIG. 3 - Sulfur Profiles in GaAs at $1003°C$ for Varying Sulfur Pressures t = 3 hours [As] = 4.5 mg/ml [S]: F-10, 6 μg/ml; F-7, 2 μg/ml; F-9, 0.6 μg/ml; F-8, 0.2 μg/ml.